Observation of a hydrogenic donor in the luminescence of electron-irradiated GaN

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Excitonic luminescence of GaN after irradiation with 0.42-MeV electrons has been investigated in detail. The low-energy irradiation generates damage exclusively in the *N* sublattice. Additional bound-exciton lines are found and are shown to arise from a hydrogenic donor with a binding energy of 25 meV. The donor binding energy, bound-exciton localization energy, and bound-exciton lifetime are discussed in comparison with the values observed for O_N and Si_{Ga} in the same sample. Nitrogen vacancies V_N forming a hydrogenic donor state are suggested to be the most likely origin of this luminescence emission. Finally, a metastable behavior related to the damage-induced defects is reported and discussed in conjunction with interstitial-nitrogen-related defects. [DOI: 10.1063/1.1570943]

Commercialization of GaN-based green to UV light emitters and potential applications of AlGaN/GaN heterostructures, such as high-power, high-frequency transistors, have drawn great attention to the basic material properties of GaN. Intrinsic defects have been the subject of many experimental and theoretical studies, since they are expected to strongly affect the optical and electrical properties of GaN. While interstitial Ga was identified by optical detection of electron–paramagnetic resonance,[1,2] Ga vacancies were detected by positron annihilation spectroscopy.[3,4] For many years, the nitrogen vacancy (V_N) was thought to account for the *n*-type conductivity of unintentionally doped GaN.[5] However, this was ruled out by first-principles calculations that revealed isolated V_N to have a high formation energy in *n*-type GaN.[6] In the present letter, we study the effect of 0.42-MeV electron irradiation of GaN, damaging exclusively the N sublattice.[7] Bound-exciton luminescence lines of a hydrogenic donor with a binding energy of 25 meV are found and tentatively attributed to V_N.

The investigated sample was a free-standing 248-μm-thick GaN layer grown at Samsung[8] by hydride vapor phase epitaxy (HVPE). Shallow donor species were found with concentrations of a few times 10^{15} cm^{-3}.[9] The irradiation to a fluence of 3×10^{17} cm^{-2} was carried out at room temperature with 0.42-MeV electrons. Time-resolved photoluminescence (TRPL) was excited with 200-fs pulses from a frequency-tripled (267 nm) mode-locked Ti: sapphire laser, dispersed with a 0.25-m single-grating monochromator, and detected with a synchroscan streak camera. The system spectral and temporal resolution was 0.05 nm and 11 ps, respectively. Cw PL measurements were performed in the near-infrared region using a HeCd laser (325 nm) for excitation and a cooled Ge diode for detection.

Figure 1 compares the integrated TRPL spectrum in the band-edge region at 5 K before and after irradiation. The main feature before irradiation is a superposition of two lines at 3.4717 and 3.4725 eV, which we assign to the oxygen-bound and silicon-bound exciton, respectively, as O_N and Si_{Ga} are the most abundant shallow donors in HVPE GaN.[10] Luminescence due to A-valence-band free excitons (X_A) is seen at 3.4782 eV, and the broad peak at 3.497 eV is related to free-exciton excited states.[11] The weak peak between the free and donor-bound exciton peaks is a B-exciton bound to neutral donors.[12]

Peaks at about 3.45 eV are bound-exciton two-electron transitions resulting from a radiative recombination process of a donor-bound exciton that goes along with an excitation of the neutral donor electron to a higher bound state. Within the effective-mass approximation, the energy separation between the donor-bound exciton and the first two-electron transition is three-fourths of the donor binding energy E_D. Since there is a significant variation in E_D among the different donor species, the two-electron transitions are a sensitive indicator of the chemical origin of the corresponding donor defect.[11] We assign the emission at 3.4512 eV to the first

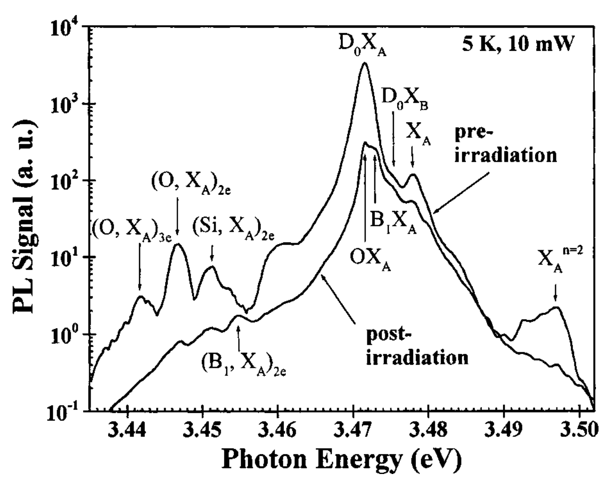

FIG. 1. Time-integrated excitonic luminescence spectra of the 250-μm free-standing HVPE GaN before and after 0.42-MeV electron irradiation.

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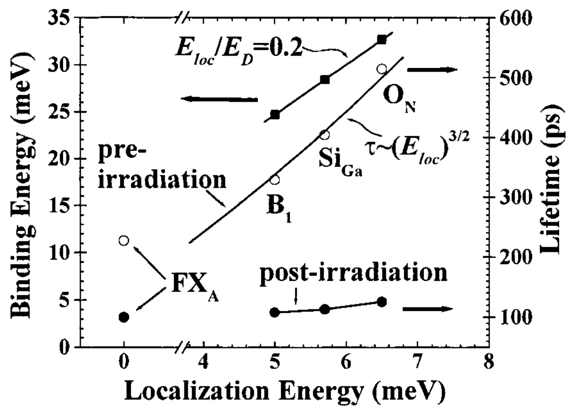

FIG. 2. Dependence of the donor binding energy E_D (solid squares) and exciton lifetime before and after irradiation (open and solid circles, respectively) on the exciton localization energy E_{loc}.

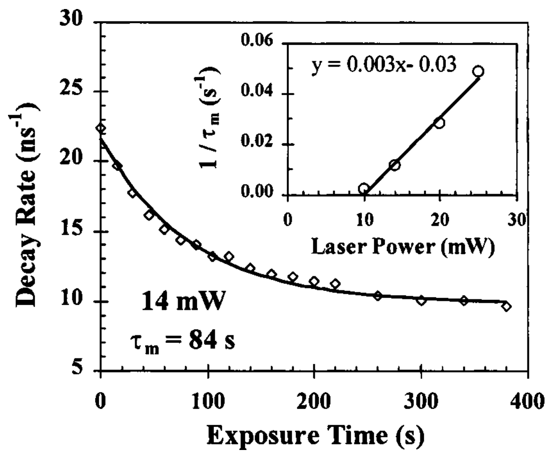

FIG. 3. Metastable behavior of the irradiated sample under focused laser exposure manifested, for example, by an exponential decrease of the inverse free-exciton lifetime (solid line: exponential fit with relaxation time constant τ_m=84 s). The inset shows a linear dependence of $1/\tau_m$ on the average laser power.

excited state of Si_{Ga}, and the 3.4472 and 3.442 eV peaks to the first and second excited states of O_N, respectively, in agreement with a recent study by Wysmolek *et al.*[13] E_D for Si_{Ga} and O_N are determined here as 28 and 33 meV, respectively. These values are in reasonable agreement with those obtained from magneto-optical studies,[14] considering that the central-cell corrections may change the three-fourths relationship slightly.[15]

After irradiation, two lines emerge, labeled B_1X_A (3.4732 eV) and $(B_1,X_A)_{2e}$ (3.4547 eV) (see Fig. 1). We assign the two lines to a bound exciton and the corresponding two-electron transition of a newly introduced shallow donor B_1, with E_D=25 meV, determined again from the peak separation. According to Haynes' empirical rule, the exciton localization energy E_{loc} (separation between the bound and free exciton lines) is proportional to E_D. In Fig. 2, we plot E_D of the donors O_N, Si_{Ga}, and B_1 versus the corresponding E_{loc}. A single proportionality factor fits all three donors, supporting the conclusion about the hydrogenic donor nature of B_1 and the assignment of the two-electron transition line. We find a value of 0.201 ± 0.002 for the proportionality constant, identical to the value of 0.2 previously reported for GaN.[16]

In addition, Fig. 2 shows the bound-exciton lifetime of B_1, Si_{Ga}, and O_N together with the lifetime of free excitons. All lifetimes, except for that of B_1 before irradiation, were obtained from a single-exponential fit of the PL decay at 5 K. The free-exciton and bound-exciton lifetime before irradiation are comparable to previously reported values.[13,17] The significant decrease of the PL decay time τ_{PL} after irradiation is attributed to a greatly reduced nonradiative lifetime τ_{nr}, in accord with the relation $1/\tau_{\mathrm{PL}}=1/\tau_{\mathrm{r}}+1/\tau_{\mathrm{nr}}$. Calculation of τ_{nr} for the O_N and Si_{Ga} transitions yields, within experimental error, the same value of about 162 ps. Using this value, the donor-bound exciton lifetime of B_1 without nonradiative recombination is estimated to be 329 ps. The donor-bound exciton lifetimes before irradiation fit Rashba–Gurgenishvili's $E_{\mathrm{loc}}^{3/2}$ relation well,[18] indicating a low concentration of nonradiative defects in the undamaged sample, and reaffirming the hydrogenic donor nature of B_1. Following the method of Henry and Nassau,[19] and accounting for the correction suggested by 't Hooft *et al.*,[20] we obtain the value of 0.456 for the free-exciton (giant) oscillator strength, corresponding to a radiative lifetime of 4.7 ns.[21] This compares well to the value of 3.3 ns for bulk GaAs.[20]

In addition to the appearance of PL lines, the irradiated sample exhibits a metastable behavior under focused 267-nm laser illumination. The laser light exposure results in a gradual transformation of the PL spectrum at 11 K. The oxygen-bound exciton intensity relative to that of the donor B_1, the total band-edge PL intensity, and the PL decay lifetime of free and bound excitons are all increasing. Eventually, a stable state is reached. The inverse lifetime of free excitons, which is a measure of the concentration of nonradiative decay channels, decreases exponentially with laser exposure time (see Fig. 3). The inverse time constant for reaching the stable state, determined from exponential fits, increases linearly with the average power of the laser in the range of 10 to 25 mW, as shown in the inset of Fig. 3. After the sample is kept in the dark at low temperature for about 30 min, the exciton lifetime decreases slightly towards the value before the prolonged laser exposure. We assume that the behavior reflects a configurational metastability and/or a recombination-enhanced dissociation and subsequent reassociation of a radiation-induced nonradiative recombination center.

In order to discuss the origin of the PL lines and the metastable behavior, we first confirm that only N atoms are displaced by 0.42-MeV electron irradiation of GaN, as was originally suggested by Look *et al.*[7] Based on the McKinley–Feshbach cross section,[22] direct displacement of Ga atoms by 0.42-MeV electrons is not expected if the assumed displacement threshold energy E_{th}(Ga) is above 20 eV. While the E_{th} have not been accurately determined for GaN, the ZnO values of about 50 eV for both sublattices[23] can be considered a good estimate due to the close similarity between ZnO and GaN in terms of the lattice constant, band gap, nuclear mass, and ionicity. Indeed, Saarinen *et al.*[4] found an introduction rate of 1 cm^{-1} for V_{Ga} with 2-MeV electron irradiation of GaN, yielding $E_{\mathrm{th}}(\mathrm{Ga})\sim45$ eV. Further support for the lack of Ga sublattice damage in our sample comes from the following observation. GaN irradiated with higher energy electrons (2.5 MeV) exhibits two broad PL bands at 0.88 and 0.95 eV, related to interstitial Ga.[1,2] However, except for a sharp peak at 0.931 eV due to the intracenter transition of residual V^{3+} (Ref. 24), we observed no luminescence in the near-infrared region. This is consistent with the finding that already at 1-MeV electron irradiation, the 0.88- and 0.95-eV bands are weak or not observable.[25] Therefore, the primary defects generated by 0.42-MeV electron irradiation are only V_N and interstitial nitrogen (N_i).

First-principles calculations[6,26] have found that N_i introduces deep levels into the GaN band gap, whereas V_N has a singly occupied p-like T_2 state resonant in the conduction band. This state autoionizes, leaving a positively charged V_N that forms a hydrogenic level. Therefore, among the possible primary damage defects, isolated V_N appears as the best candidate for the donor signature observed here. As outlined in the following, this assignment is also consistent with the defect migration reactions to be expected during the irradiation, which in addition provides a possible clue about the observed metastability. A recent first-principles calculation[27] shows that V_N is immobile compared with N_i. Therefore, V_N is expected to persist after irradiation at room temperature, while the more mobile N_i may get trapped at impurities or other defects in the material. O_N and Si_{Ga} are the most likely traps in the present material, resulting in donor-deactivating complexes N_i–O_N and/or N_i–Si_{Ga}. In this framework, the observed metastability may be attributed to a partial or full dissociation of N_i from the donor impurities, which may be driven by carrier recombination through the complexes during illumination. This would naturally explain the increased luminescence from O_N-(and Si_{Ga})-bound excitons after (partial) dissociation of the proposed N_i–O_N and/or N_i–Si_{Ga} complexes.

Final support for the assignment of the hydrogenic donor to V_N comes from an assessment of the central-cell effects on E_D. Moore *et al.*[14] derived E_D from effective-mass theory for GaN without central-cell corrections to be 29.1 meV. While O_N was found to have E_D a little higher than this, indicating an attractive core correction that leads to a stronger localization of the donor electron wave function at the core, the low ionization energy of the donor B_1 reported here means a repulsive core correction. This is reasonable since the positive charge on V_N is distributed over the electron states of the surrounding Ga atoms, resulting in a fairly delocalized wave function and thus requiring less energy for the ionization.

In a previous study,[7] a 64-meV donor and an acceptor with identical concentrations were found to be introduced by electron irradiation, and they were tentatively assigned to V_N and N_i, respectively. The donor level was later also observed with deep-level transient spectroscopy.[28] However, in this case, higher electron energies (0.7–1 MeV) and higher dopant concentrations were used. Therefore, the observed levels might be due to other defects.

In summary, excitonic luminescence of GaN after irradiation with 0.42-MeV electrons was studied. The irradiation was shown to generate damage exclusively in the N sublattice. Bound-exciton lines arising from a hydrogenic donor with binding energy 25 meV were tentatively assigned to the N vacancy. The bound-exciton localization energy and lifetime were discussed in conjunction with the values observed for O_N and Si_{Ga} in the same sample. Finally, a metastable behavior related with the damage-induced defects was reported and tentatively explained in the framework of nonradiative defect complexes involving N_i.

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